Highly efficient SERS nanowire/Ag composites

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Introduction: Optically based sensing provides advantages over electronic sensing because optical spectra can uniquely finger print a chemical compound, significantly reducing false alarms and simplifying the detection process. In addition, light can easily be directed over long distances, enabling remote sensing. In Raman scattering (RS), light is scattered from a chemical of interest and the vibrational modes in the chemical red shift the frequency of the scattered light, producing a spectrum of lines that are characteristic of that molecule. A major issue for ordinary Raman scattering is that its cross-sections are very small, resulting in low sensitivity (1E-8 of the intensity of the exciting laser). For most solids and liquids, this is not a problem because of the large numbers of molecules or atoms that are exposed to the laser light. In the case of trace amounts of molecules in gases or liquids, detection through ordinary Raman scattering is virtually impossible. However, the Raman signal can be enhanced by many orders of magnitude by the use of metal nano particles[1], which is referred to as surface enhanced Raman scattering (SERS). The SERS enhancement of molecules adsorbed on the roughened metal surface is caused by local electromagnetic fields that are created by the laser excitation of surface plasmons at the metal surface. In addition, it has been shown that local hot spots in the electric fields produced by interactions of localized plasmons on adjacent or neighboring nanoparticles can produce even larger SERS effects[2]. Unfortunately, although the SERS effect has been recognized for a long time, a full understanding of the phenomenon has not yet been achieved. This lack of understanding

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limits its application potential, in that it is difficult to produce highly sensitive, inexpensive and highly repeatable SERS substrates. To address these issues, we have developed a new SERS substrate material, consisting of dielectric/Ag metal shell nanowires, which exhibit high SERS sensitivity due to their plasmonic coupling. They are also sensitive at low concentrations, quite repeatable, and inexpensive to produce.

Technical Approach: The growth of the Ga_2O_3 nanowires was performed by the vapor-liquid-solid (VLS) growth in a tube furnace, using Si(100) and Si(111) substrates and a 20 nm Au film[3]. Ga ((99.995% purity) and oxygen were used as the source material and the growth was performed at 900°C at a vacuum of 10^{-2} Torr. The Ag shell coating was deposited via e-beam evaporation under high vacuum conditions. The SERS sensitivity of the nanowire substrates has been determined using Rhodamine 6G/methanol and DNT/methanol dilutions. The Ga_2O_3/Ag nanowire composite substrates are shown in Figure 1a. As can be seen, they consist of a dense random 3D network of crossed wires. A comparison of the SERS signal from 0.2 picograms of Rh6G for the nanowire composite substrates and a commercially available SERS substrate from Mesophotonics (Klarite) is shown in Figure 1b. As shown, no SERS signal is evident in the case of the commercial Mesophotonics sample, while a strong SERS signal is clearly seen for the nanowire composites. From these results, the nanowire/Ag composite substrate can repeatably exhibit an enhancement which is roughly two orders of magnitude higher than the commercially available SERS substrate.

The SERS of Rh6G, using the nanowire/metal random 3D arrays, has also been measured to be several orders of magnitude more sensitive than other SERS substrates, such as Ag nanosphere arrays produced by the Tollen's reaction, SiO_2/Ag nanosphere composites, polystyrene/Ag nanosphere composites, as well as roughened metal surfaces. In addition, these wires have exhibited sensitivity to DNT (which has a very low vapor pressure and is thus difficult to detect) better than picograms (shown in Figure 2), which is in fact the first reported SERS measurement of DNT using Ag metal nanostructures.

Furthermore, these nanowire composites can easily be removed from the substrate by sonication in an ethanol solution, and they show an enhanced SERS signal even when deposited in a significantly dilute form. This opens up the possibility of covert tagging and tracking applications.

The most intriguing result from this work indicates that randomly crossed wires increase the SERS enhancement in the vicinity of the regions where wires cross, as shown in Figure 3a. The effect on the plasmon resonance by wire crossings can be modeled using a finite element Comsol simulation of the electric field near two 45 nm diameter Ag crossed wires in response to light polarized in the x-direction (Figure 3a). The crossing of the nanowires leads to coupled plasmonic behavior that spatially extends the sensitivity of the nanowires to encompass the regions between the wires and significantly beyond the wires. This would not only enhance the SERS effect due to the strong coupling, but allow more molecules to enter this high electric field region, thereby enhancing the SERS sensitivity. In the case of two Ag nanosphere of the same diameter, the enhancement spatial extent is significantly smaller, as shown in Figure 3b. In addition, the nanosphere geometries require a very specific spacing in order to maximize the enhancement due to coupling, which is not the case in crossed wires, since an optimal spacing is always present for every crossing angle due to the wire geometry. As a simple rule of thumb, the sensitivity regions for the wires are within a sphere whose diameter is the length of the longest wire, which is a significant improvement over nanosphere-type SERS substrates.

Conclusion: Randomly oriented Ga_2O_3/Ag nanowire networks have been formed and we have shown that these substrates results in highly sensitive SERS signals using Rhodamine 6G as well as DNT. It is suggested that this SERS sensitivity is due to the formation of a large number of “hot” spots (enhanced electric fields due to plasmon coupling) when arranged in a random crossing geometry. Finite element calculations show significantly enhanced electric fields in the regions of the wire crossing, as well as surrounding the crossed wires, in support of the experimental results.

Due to these highly efficient “hot” spot regions formed by the crossing of the nanowires, we have also demonstrated that large SERS enhancements are possible even when the density of the nanowire network is significantly reduced. Since these wires can be deposited at low concentrations on any substrate and any size area, they have potential in applications such as large area sensor arrays, covert tagging and remote sensing.

References:

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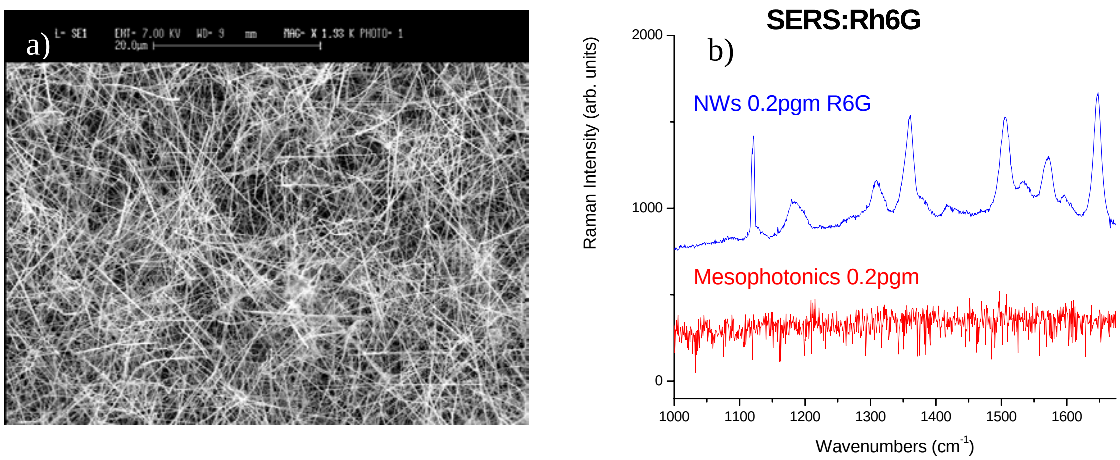
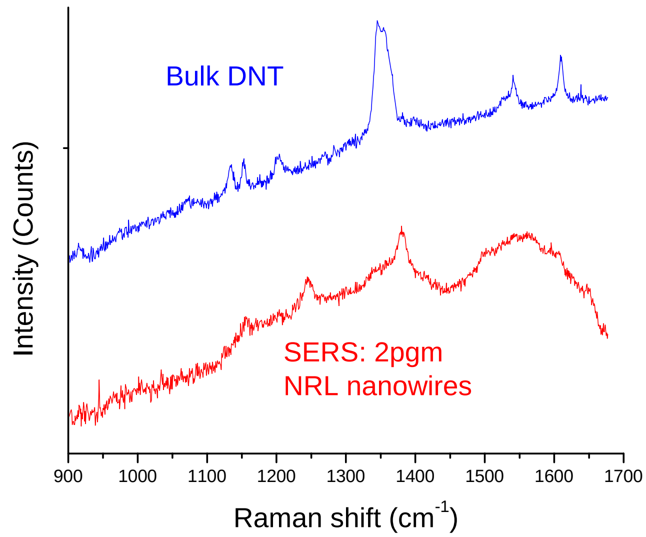
Figure Captions:

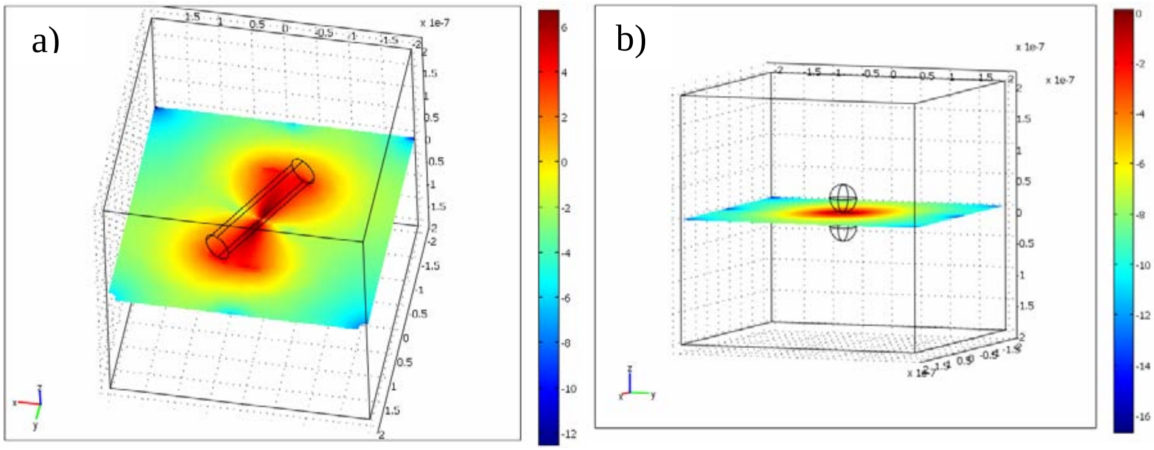
Figure 1. (a) Ga_2O_3 core/Ag shell nanowire composite and (b) comparison of SERS signal for Mesophotonics “Klarite” commercial substrate and Ga_2O_3/Ag nanowires.

Figure 2. Raman spectrum of bulk DNT and a SERS spectrum of 2 picograms of DNT obtained from the dielectric/Ag nanowires.

Figure 3. Comsol electric field simulations for a) Ag crossed nanowires and b) same diameter Ag nanospheres. Note the much larger area of enhancement in the case of the nanowires.


a)
L= SE1 ENT= 7.00 KV WD= 9 mm MAG= X 1.33 K PHOTO= 1
20.0µm
b)
SERS:Rh6G
NWs 0.2pgm R6G
Mesophotonics 0.2pgm
Raman Intensity (arb. units)
Wavenumbers (cm-1)
2000
1000
0
1000
1100
1200
1300
1400
1500
1600


Bulk DNT
SERS: 2pgm
NRL nanowires
Intensity (Counts)
900
1000
1100
1200
1300
1400
1500
1600
1700
Raman shift (cm-1)



a)
x 1e-7
6
4
2
0
-2
-4
-6
-8
-10
-12
b)
x 1e-7
0
-2
-4
-6
-8
-10
-12
-14
-16